June 24, 1997

Ms. Debra Rossi (3HW23)
Remedial Project Manager
U.S. Environmental Protection Agency, Region III
841 Chestnut Street
Philadelphia, Pennsylvania 19107-4431

Woodlawn Landfill Site
Remedial Design/Remedial Action
Administrative Order, EPA Docket No. III 95-05-OC
Cecil County, Maryland

Dear Ms. Rossi:

As you requested on June 17, 1997, this letter is to provide supplemental information regarding the following:

1. additional information to allow a more direct comparison of published leachate indicator data (such as TOC, BOD, and COD) for landfills to the reported concentrations of these indicators in groundwater at the Woodlawn site.

2. tables summarizing analytical results for all groundwater samples collected in February and March 1997.

3. a comprehensive summary of results for all groundwater samples collected in February and March 1997 that were analyzed for polynuclear aromatic hydrocarbons (PAHs) and pentachlorophenol using methods that afford lower detection limits.

4. vinyl chloride and analytical holding times.

At this time, we have not completed efforts to develop additional data that provides a more direct comparison of leachate indicator data (Item 1 above). Once the efforts to acquire additional information are complete, we will provide the additional information to USEPA. At this time, we have not completed efforts to develop additional data that provides a more direct comparison of leachate indicator data (Item 1 above). Once the efforts to acquire additional information are complete, we will provide additional information to USEPA. As we understand it, the essential question regarding

this issue is: "How much would leachate from the landfill be diluted in groundwater, as compared to leachate exuding directly from waste material"? Unfortunately, there is no readily available data upon which to make this determination; however, the groundwater data from Woodlawn provides insight if viewed in the context of data from residential wells surrounding the landfill. Generally, the concentration of landfill leachate indicator parameters are not significantly higher in the most heavily-affected wells on site compared to surrounding residential wells. These empirical data demonstrate that the leachate generation rate at Woodlawn is not significantly greater than the assimilative capacity of the biogeochemical ecosystem surrounding the landfill.

Tables summarizing preliminary analytical results for the February-March 1997 groundwater samples (Item 2 above) were previously provided to USEPA in the June 3, 1997 Technical Memorandum (see Attachment D of the June 3, 1997 response to USEPA comments on the predesign). The validated data reports for these samples were included in the May 1997 progress report submitted to USEPA. A partial summary (natural attenuation monitoring wells only) of PAH and PCP analytical results for groundwater samples collected in February and March 1997 was previously provided to USEPA in the June 3, 1997 Technical Memorandum (Item 3). A comprehensive summary of PAH and PCP analytical results for these samples is provided in the attached Table 1. The topic of vinyl chloride concentrations and analytical holding times (Item 4) is thoroughly discussed herein.

VINYL CHLORIDE AND ANALYTICAL METHODOLOGY

As documented, a significant reduction in the concentration, extent and mass of vinyl chloride has been observed at the Woodlawn Landfill site. Historical groundwater sampling data collected since 1982 at the site indicates that the concentrations of dissolved vinyl chloride in individual monitoring wells has markedly declined since 1987. Typical reductions in concentration are, for example, 74 percent in well F-5, 96 percent in well F-6, 99 percent in well F-7, and 77 percent in well F-10.

A careful evaluation of biogeochemical data recently collected at the site has led to the demarcation of three zones of biogeochemical activity: an anaerobic-reducing zone; a more oxidizing, or transitional zone; and an aerobic zone. The observed vinyl chloride mass reduction is a result of the cumulative effects of the oxidation of vinyl chloride via predominantly anaerobic mechanisms in the interior portions of the plume, a combination of anaerobic and aerobic mechanisms in the transition zone, followed by the rapid oxidation of vinyl chloride by dissolved oxygen in the aerobic zones present at the outer edges of the plume.

USEPA has inquired about information on historical sample holding times and vinyl chloride concentrations in groundwater samples collected at the Woodlawn site. Apparently USEPA's inquiry is in reaction to a study that reports potential losses of vinyl

chloride that may occur within the USEPA-mandated 14-day analytical holding time for preserved water samples. Therefore, this letter addresses the potential losses of vinyl chloride that may occur within the 14-day analytical holding time, and whether that could reasonably be a factor in the observed historical reduction of vinyl chloride in groundwater that has been documented at the site. Our conclusion is that any potential losses of vinyl chloride that could be related to analytical holding times are not significant and are far exceeded by the observed declining trends and reduced extent and mass of vinyl chloride in groundwater at the Woodlawn site. Furthermore, the uniform logarithmic decline rate in vinyl chloride concentrations in many wells is characteristic of natural attenuation, and could not have been reproduced by somewhat random variations in laboratory holding times.

GENERAL OVERVIEW

In response to USEPA's inquiry about analytical holding time, Geraghty & Miller acquired two published studies that speak to the issue but draw opposite conclusions. The first study was published by the Minnesota Department of Health (MDH) and concluded there are measurable losses of vinyl chloride within analytical holding times (Soule, et al., 1996). The second study was published in the American Environmental Laboratory and found that holding times could actually be increased from 14 days to 28 days for the analysis of volatile organics in water samples because of no percent change in vinyl chloride concentration was measured after a holding time of 28 days in either a 20 part per billion spiked sample or a 200 part per billion spiked sample (West, et al., 1997).

In 1996, the MDH published a study on vinyl chloride loss during laboratory holding time (Soule, et al., 1996). This study investigated the current holding time of 14 days to determine if vinyl chloride is lost during this time. The focus of the study was on samples that contained very low initial concentrations, 2 micrograms per liter (ug/L) and less, of vinyl chloride. The study reported 30 percent losses of vinyl chloride in these low concentrated samples; with 25 percent of the losses occurring within the first 2 days. Also, this study recognized the variability that is inherent in reported results for vinyl chloride at low concentrations.

The American Environmental Laboratory, April 1997 edition, published a study that contradicts the conclusions of the MDH study. One distinction between the two studies is that the MDH study focused on low concentrations of vinyl chloride, whereas, the latter study focused on holding time effects in samples with concentrations on the order of 20 ug/L and 200 ug/L. The American Environmental Laboratory found the scientific basis for actually increasing holding times from 14 days to 28 days for the analysis of volatile organics in water samples. The study concludes that a 28 day holding time would not jeopardize the measurement of volatile organics in water samples. In that study, no percent change in vinyl chloride concentration was measured after a holding

time of 28 days in either a 20 part per billion spiked sample or a 200 part per billion spiked sample (West, et al., 1997).

Furthermore, it is important to view the reported losses attributed to holding times in the context of the inherent variability in the analytical methodology. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846) provides the USEPA approved methods for obtaining data to satisfy requirements of 40 CFR Parts 122 through 270 and presents the accepted standard routine analytical methodology. In SW-846, the published calibration and quality control acceptance criteria for USEPA Method 8240B for volatile organics reports a range for percent recovery measured from detection to 251 percent for vinyl chloride. This wide range in percent recovery measured was derived assuming a sample vinyl chloride concentration of 20 ug/L and is based on actual method performance data. Therefore, the inherent variability reflected in the calibration and QC acceptance criteria for the approved analytical methodology far outweighs any potential losses that may be attributed to holding times.

SITE SPECIFIC DATA

As requested by USEPA, provided in Table A and B below are summaries of the vinyl chloride concentration and holding time data for wells F-5, F-6, F-7, and F-10 for samples collected in March 1990 and in March 1996. Data for wells F-5, F-6, F-7, and F-10 have been provided because these historical data have been repeatedly presented to USEPA as best illustrating the declining vinyl chloride concentration trends in groundwater at the site. The trends for vinyl chloride in these wells are shown on Figures 1A through 1D.

Table A. Vinyl Chloride and Holding Times 1990

Well Identification	Date Sampled	Date Analyzed	Holding Time (Days)	Vinyl Chloride Concentration (ug/L)
F-5	3/14/90	3/20/90	6	110
F-6	3/14/90	3/20/90	6	520
F-7	3/13/90	3/15/90	2	57
F-10	3/12/90	3/15/90	2	27

*   Sample/analysis control documents prepared by IT indicate samples may not have been preserved with hydrochloric acid.

Table B. Vinyl Chloride and Holding Times 1996

Well Identification	Date Sampled	Date Analyzed	Holding Time (Days)	Vinyl Chloride Concentration (ug/L)
F-5	3/14/96	3/25/96	11	35
F-6	3/14/96	3/20/96	6	110
F-7	3/12/96	3/26/96	14	1.2
F-10	3/11/96	3/23/96	12	13

*   All samples were preserved with hydrochloric acid to inhibit sample degradation.

All samples presented in Tables A and B were analyzed within the USEPA mandated 14-day holding time for volatile organic analyses of preserved water samples; therefore all analytical results are valid and defensible. Three samples (F-5, F-7, and F-10) that were analyzed in March 1990 have a relatively shorter holding time than samples analyzed in 1996. A likely explanation for the shorter holding times for the March 1990 samples is that sample/analysis control documents prepared by IT indicate these samples may not have been preserved with hydrochloric acid. Therefore, the laboratory may have hastened the analyses of these nonpreserved samples to preclude possible in-sample biodegradation of vinyl chloride. The preservation of water samples using hydrochloric acid is a normal procedure employed to inhibit possible sample degradation. Thus, it's plausible that the March 1990 samples could have degraded, while awaiting analysis, more than the March 1996 samples. The March 1990 concentrations could be biased low; so, the percent reduction between the two events could be greater than is evident. This illustrates a few of the many variables that need to be accounted for in any field study to isolate possible effects on analytical results related to hold time.

Samples collected from Well F-6 in March 1990 and March 1996 were both analyzed six days after sample collection. These results indicate approximately 80 percent reduction in vinyl chloride concentrations between these two sample events. Given that these samples were analyzed within the same holding time period and that the March 1996 sample was preserved whereas, the March 1990 sample was not, these data empirically demonstrate that potential losses related to analytical holding times are not a factor in the observed reduction in vinyl chloride. Regardless for reasons cited above, any losses that may occur within USEPA mandated holding times are insignificant and certainly do not factor in the documented declining trends, reduced areal extent and mass of vinyl chloride in groundwater at the Woodlawn Site.

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SUMMARY

A preponderance of empirical data demonstrate a significant reduction in concentration, aereal extent, and mass of vinyl chloride at the Woodlawn site. Historical biogeochemical data and the more recent biogeochemical data, collected following USEPA sampling and analytical protocols for evaluating natural attenuation of chlorinated solvents in groundwater, have confirmed natural degradation mechanisms as a predominant reason for the observed reductions. The MDH study which has been published relating possible losses of vinyl chloride to analytical holding times does not lead to a concern that these possible losses are a significant factor in the observed declining concentration trends and reductions of vinyl chloride in groundwater at the Woodlawn site. This conclusion is based on the following:

1.   The focus of the aforementioned study was on samples with very low (1.5 and 2 ug/L) initial concentrations of vinyl chloride. The declining trends and reductions of vinyl chloride observed at the Woodlawn site involve concentrations of vinyl chloride that were once orders of magnitude higher than those in that study. The historical concentrations have shown an initial rise to a peak followed by a declining trend with time that is predictable and consistent with the knowledge and understanding of natural attenuation mechanisms and site characteristics (see Figures 1A through 1D).

2.   Other related studies have concluded there is sufficient scientific basis for increasing holding times from 14 days to 28 days for the analysis of volatile organics in water samples. In one such study, no percent change in vinyl chloride concentration was measured after a holding time of 28 days in either a 20 part per billion spiked sample or a 200 part per billion spiked sample (West, et al., 1997).

3.   Potential losses attributed to holding times must be considered in the context of the inherent variability of the analytical methodology. In SW-846, the published calibration and quality control acceptance criteria for USEPA Method 8240B for volatile organics reports a range for percent recovery measured from detection to 251 percent for vinyl chloride. The inherent variability reflected in the calibration and QC acceptance criteria for the approved analytical methodology far outweighs any potential losses that may be attributed to holding times.

4.   The magnitude of observed reductions in vinyl chloride between the March 1990 and March 1996 sampling events far exceed any possible losses that

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could theoretically be attributed to differences between sample holding times. In fact, samples collected from Well F-6 in March 1990 and March 1996 were both analyzed six days after sample collection. Given that these samples were analyzed within the same holding time period and that the March 1996 sample was preserved whereas, the March 1990 sample was not, these data empirically demonstrate that potential losses related to analytical holding times are not a factor in the observed reduction (in this case 80 percent or more) in vinyl chloride.

As demonstrated herein, any potential losses of vinyl chloride that could be related to analytical holding times are indistinguishable from other sampling and analysis variables; not significant and are far exceeded by the observed declining trends and reduced extent and mass of vinyl chloride due to natural attenuation at the Woodlawn site; and are not significant in the context of the goals and objectives nor the interpretation of groundwater analytical results at the Woodlawn site.

We hope that the information and discussion that we have provided herein sufficiently respond to your requests and we look forward to hearing from you shortly regarding USEPA's decision regarding the groundwater remedy at the Woodlawn site. If you have any questions or should you require additional information, please call.

Sincerely,
GERAGHTY & MILLER, INC.

Jeffrey A. Smith
Project Manager

Suthan S. Suthersan, Ph.D., P.E.
Project Officer

c: Tim Bent, Bridgestone/Firestone

Figures

Figure 1A.   Declining Trends for Vinyl Chloride Versus Sodium in F-5, Woodlawn Landfill, Cecil County, Maryland.

Figure 1B.   Declining Trends for Vinyl Chloride Versus Sodium in F-6, Woodlawn Landfill, Cecil County, Maryland.

Figure 1C.   Declining Trends for Vinyl Chloride Versus Sodium in F-7, Woodlawn Landfill, Cecil County, Maryland.

Figure 1D.   Declining Trends for Vinyl Chloride Versus Sodium in F-10, Woodlawn Landfill, Cecil County, Maryland.

Attachments

Table 1   Summary of Validated Analytical Results for Groundwater Samples Collected from Monitoring Wells on February 26 through March 10, 1997, Woodlawn Landfill, Cecil County, Maryland.

REFERENCES

USEPA-SW-846, 1986, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Revision 2, September 1994.

Soule, R. et al., 1996. Vinyl Chloride Loss During Laboratory Holding Time, Regulatory Toxicology and Pharmacology 23, pp. 209-212.

West, O.R. et al., 1997. A Scientific Basis for Revising Regulatory Holding Times for VOC Water Samples. American Environmental Laboratory, April 1997.

Table 1. Summary of Validated Analytical Results for Groundwater Samples Collected from Monitoring Wells on February 26 through March 10, 1997, Woodlawn Landfill, Cecil County, Maryland.

Location ID	B-2	B-3	B-4	B-5	B-6	F-1	F-10	F-2	F-2 DUP	F-3
SAMPDATE	3/4/97	3/5/97	3/5/97	3/6/97	3/6/97	2/27/97	3/7/97	3/10/97	3/10/97	3/6/97
Benzo(A)Anthracene	.008 UL	.008 U	.008 UL	.008 UL	.008 U	.008 U	.008 UL	.008 U	0.07	.008 U
Benzo(A)Pyrene	.004 UL	.004 U	.004 UL	.004 UL	.004 U	.004 U	.004 UL	.004 U	0.08	.004 U
Benzo(B)Fluoranthene	.006 UL	.006 U	.006 UL	.006 UL	.006 U	.008 J	.006 UL	.010 J	0.1	.006 U
Benzo(K)Fluoranthene	.002 UL	.002 U	.002 UL	.002 UL	.002 U	.002 U	.002 UL	.007 J	0.1	.002 U
Chrysene	.04 UL	.04 U	.04 UL	.04 UL	.04 U	.04 U	.04 UL	.04 U	.09 J	.04 U
Pentachlorophenol	.005 UL	.005 U	.005 UL	.005 UL	.03 U	.005 U	.03 UL	.03 U	.03 U	.05 U

U   Compound was analyzed for but not detected, method detection limit reported.
L   The associated numerical value is an estimated value.
J   The associated numerical value is an estimate.
DUP   Field duplicate sample.

Table 1. Summary of Validated Analytical Results for Groundwater Samples Collected from Monitoring Wells on February 27 through March 10, 1997, Woodlawn Landfill, Cecil County, Maryland.

Location ID	F-5	F-6	F-8	F-9	ITB-1	ITB-2	ITB-3	ITB-4	ITB-4 DUP	ITB-5
SAMPDATE	3/6/97	3/10/97	3/10/97	3/7/97	3/7/97	3/5/97	3/6/97	3/6/97	3/6/97	3/6/97
Benzo(A)Anthracene	.008 U	.008 U	.008 U	.008 UL	.008 UL	.008 U	.008 UL	.008 UL	.008 UL	.008 U
Benzo(A)Pyrene	.004 U	.004 U	.004 U	.004 UL	.004 UL	.004 U	.004 UL	.004 UL	.004 UL	.004 U
Benzo(B)Fluoranthene	.006 U	.006 U	.006 U	.006 UL	.006 UL	.006 U	.006 UL	.006 UL	.006 UL	.006 U
Benzo(K)Fluoranthene	.002 U	.002 U	.002 U	.002 UL	.002 UL	.002 U	.002 UL	.002 UL	.002 UL	.002 U
Chrysene	.04 U	.04 U	.04 U	.04 UL	.04 UL	.04 U	.04 UL	.04 UL	.04 UL	.04 U
Pentachlorophenol	.03 U	.03 U	.005 U	.03 UL	.03 UL	.005 U	.005 UL	.005 R	.03 UL	.03 U

U   Compound was analyzed for but not detected, method detection limit reported.

L   The associated numerical value is an estimated quanity, possibly biased low.

J   The associated numerical value is an estimate.

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Table 1. Summary of Validated Analytical Results for Groundwater Samples Collected from Monitoring Wells on February 27 through March 10, 1997, Woodlawn Landfill, Cecil County, Maryland.

Location ID	ITB-6	ITP-1	ITP-1 DUP	ITP-2	ITP-3	ITS-1	MW-101A	MW-101B	MW-102A	MW-103A
SAMPDATE	3/6/97	3/7/97	3/7/97	2/28/97	2/27/97	2/28/97	3/7/97	3/10/97	2/28/97	3/5/97
Benzo(A)Anthracene	.008 U	.008 UL	.008 UL	0.02	.008 U	.008 U	.008 UL	.008 U	.008 U	.008 UL
Benzo(A)Pyrene	.004 U	.004 UL	.004 UL	.004 U	.004 U	.004 U	.004 UL	.004 U	.004 U	.004 UL
Benzo(B)Fluoranthene	.006 U	.006 UL	.006 UL	.006 U	.006 U	.006 U	.006 UL	.006 U	.006 U	.006 UL
Benzo(K)Fluoranthene	.002 U	.002 UL	.002 UL	.002 U	.002 U	.002 U	.002 UL	.002 U	.002 U	.002 UL
Chrysene	.04 U	.04 UL	.04 UL	.04 U	.04 U	.04 U	.04 UL	.04 U	.04 U	.04 UL
Pentachlorophenol	.008 B	.005 UL	.03 UL	.005 U	.005 U	.005 U	.005 UL	.007 J	.005 U	.005 U

Handwritten annotations in left margin: 6.13, 0.03, 0.7, 0.7, 1.5, 1

U Compound was analyzed for but not detected, method detection limit reported.

L The associated numerical value is an estimated quanity, possibly biased low.

J The associated numerical value is an estimate.

DUP Field duplicate sample.

AR309668

Table 1. Summary of Validated Analytical Results for Groundwater Samples Collected from Monitoring Wells on February 27 through March 10, 1997, Woodlawn Landfill, Cecil County, Maryland.

Location ID	MW-104A	MW-105A	MW-105B	MW-106A	MW-106B	MW-107A	MW-108A	MW-108B	MW-109A	MW-109B
SAMPDATE	2/26/97	3/5/97	3/7/97	3/4/97	3/5/97	2/26/97	2/27/97	3/4/97	3/4/97	3/4/97
Benzo(A)Anthracene	.008 U	.008 U	.008 UL	.008 U	.008 U	.008 U	.008 U	.008 U	.008 U	.008 U
Benzo(A)Pyrene	.004 U	.004 U	.004 UL	.004 U	.004 U	.004 U	.004 U	.004 U	.004 U	.004 U
Benzo(B)Fluoranthene	.014 B	.006 U	.008 UL	.006 U	.006 U	.006 U	.006 U	.021 J	.006 U	.006 U
Benzo(K)Fluoranthene	.002 U	.002 U	.002 UL	.002 U	.002 U	.002 U	.002 U	.002 U	.002 U	.002 U
Chrysene	.04 U	.04 U	.04 UL	.04 U	.04 U	.04 U	.04 U	.04 U	.04 U	.04 U
Pentachlorophenol	.005 U	.005 U	.005 UL	.016 J	.005 U	.005 U	.005 U	.005 U	.005 U	.005 U

U   Compound was analyzed for but not detected, method detection limit reported.

L   The associated numerical value is an estimated quanity, possibly biased low.

J   The associated numerical value is an estimate.

DUP   Field duplicate sample.

Table 1. Summary of Validated Analytical Results for Groundwater Samples Collected from Monitoring Wells on February 27 through March 10, 1997, Woodlawn Landfill, Cecil County, Maryland.

Location ID	MW-109B DUP	OW-1	OW-2	OW-4	SW-1	SW-1 DUP	TSTA-1	WW-1
SAMPDATE	3/4/97	3/3/97	3/3/97	2/27/97	2/26/97	2/26/97	3/4/97	2/28/97
Benzo(A)Anthracene	.008 U	.008 U	.008 U	.008 U	.008 U	.008 U	.008 U	.008 UL
Benzo(A)Pyrene	.004 U	.004 U	.004 U	.004 U	.004 U	.004 U	.004 U	.004 UL
Benzo(B)Fluoranthene	.006 U	.006 U	.006 U	.006 U	.006 U	.006 U	.006 U	.006 UL
Benzo(K)Fluoranthene	.002 U	.002 U	.002 U	.002 U	.002 U	.002 U	.002 U	.002 UL
Chrysene	.04 U	.04 U	.04 U	.04 U	.04 U	.04 U	.04 U	.04 UL
Pentachlorophenol	.005 U	.005 U	.005 U	.005 U	.005 U	.005 U	.005 U	.005 U

U   Compound was analyzed for but not detected, method detection limit reported.
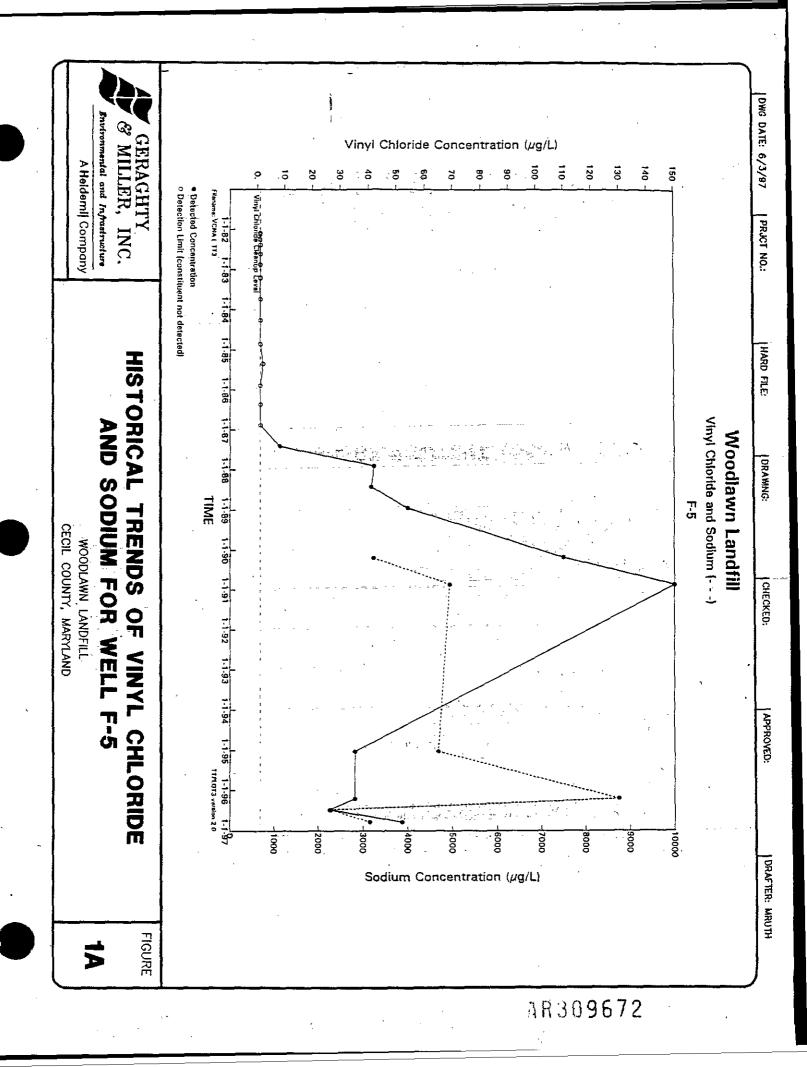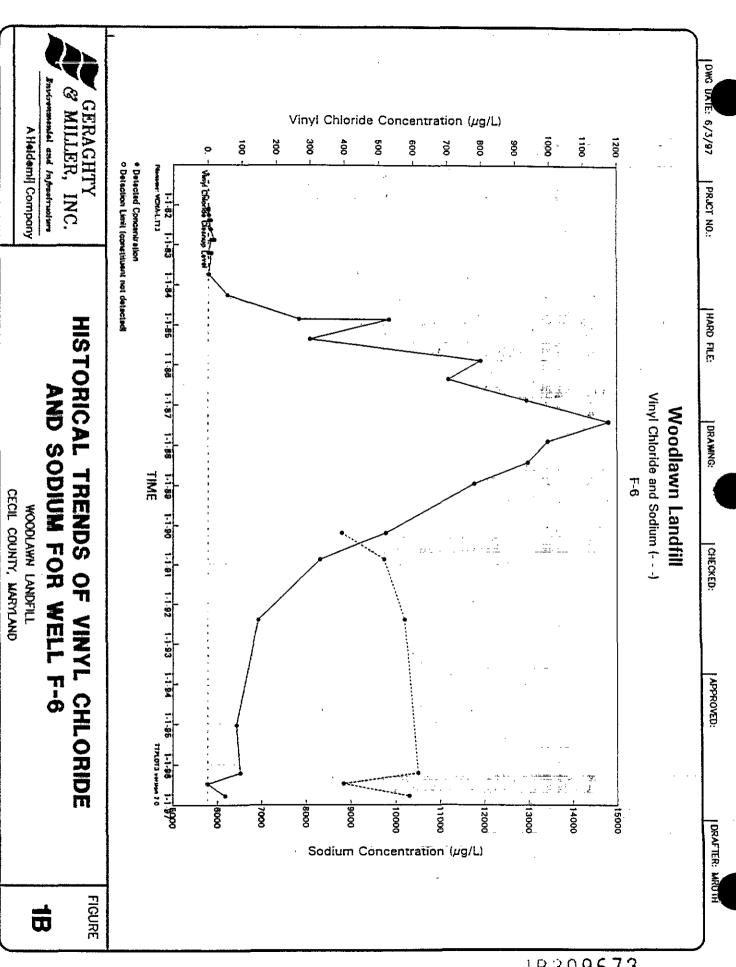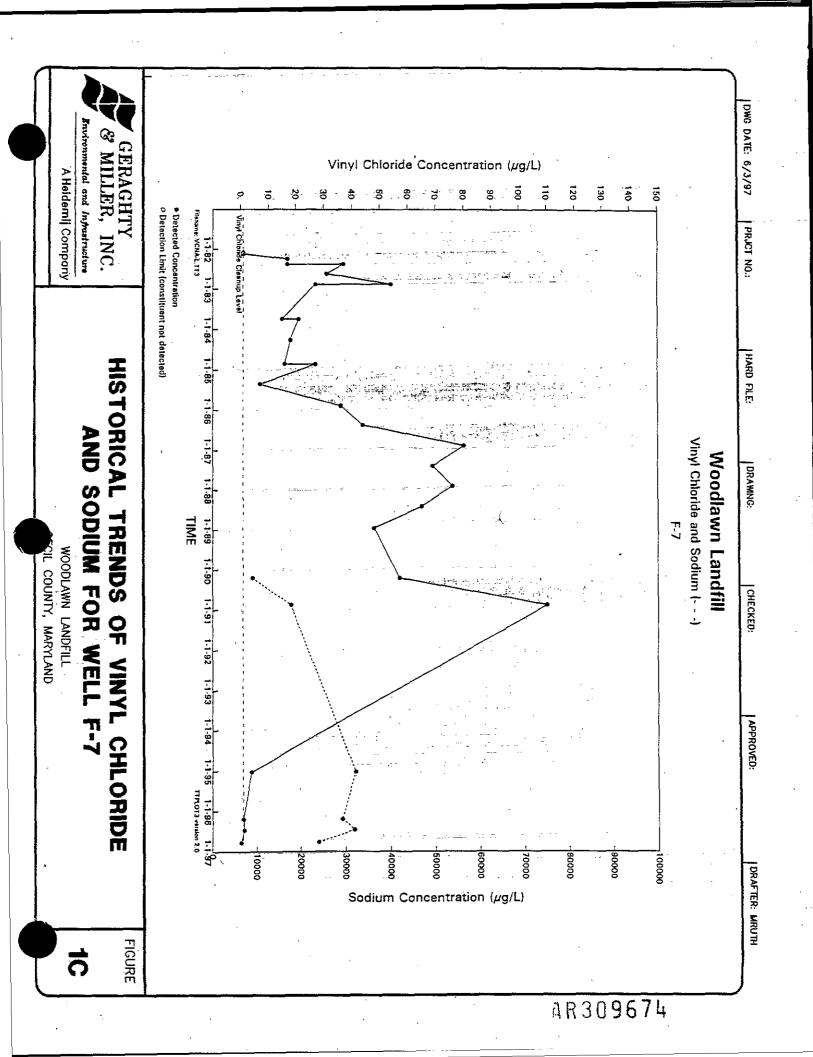L   The associated numerical value is an estimated quanity, possibly biased low.
J   The associated numerical value is an estimate.
DUP Field duplicate sample.

Table 1. Summary of Validated Analytical Results for Groundwater Samples Collected from Monitoring Wells on February 27 through March 10, 1997, Woodlawn Landfill, Cecil County, Maryland.

Location ID	FB-1'	FB-2'	FB-3'	FB-4'	FB-5'	FB-6'	FB-7'	FB-8'	FB-9'
SAMPDATE	2/26/97	2/27/97	2/28/97	3/3/97	3/4/97	3/5/97	3/6/97	3/7/97	3/10/97
Benzo(A)Anthracene	.008 J	.008 U	.008 U	.008 U	.008 U	.015 J	.008 U	.008 UL	.008 U
Benzo(A)Pyrene	.009 J	.004 U	.004 U	.004 U	.004 U	.029 J	.004 U	.004 UL	.004 U
Benzo(B)Fluoranthene	.006 U	.006 U	.006 U	.006 U	.006 U	.035 J	.006 U	.006 UL	.006 U
Benzo(K)Fluoranthene	.012 J	.002 U	.002 U	.002 U	.002 U	.019 J	.002 U	.002 UL	.002 U
Chrysene	.04 U	.04 U	.04 U	.04 U	.04 U	.05 J	.04 U	.04 UL	.04 U
Pentachlorophenol	.005 U	.005 U	.005 U	.005 U	.005 U	.006 J	.005 U	.005 UL	.005 U

U Compound was analyzed for but not detected, method detection limit reported.

L The associated numerical value is an estimated quanity, possibly biased low.

J The associated numerical value is an estimate.

DUP Field duplicate sample.

   Field rinsate blank sample.

GERAGHTY & MILLER, INC.

Woodlawn Landfill
Vinyl Chloride and Sodium (- -)
F-5

Vinyl Chloride Concentration (µg/L)

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Vinyl Chloride Cleanup Level

Filename: VCMAL 113

• Detected Concentration
○ Detection Limit (constituent not detected)

1-1-82 1-1-83 1-1-84 1-1-85 1-1-86 1-1-87 1-1-88 1-1-89 1-1-90 1-1-91 1-1-92 1-1-93 1-1-94 1-1-95 1-1-96 1-1-97

TIME

TIPLOT3 version 2.0

Sodium Concentration (µg/L)

1000 2000 3000 4000 5000 6000 7000 8000 9000 10000

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HISTORICAL TRENDS OF VINYL CHLORIDE
AND SODIUM FOR WELL F-5

WOODLAWN LANDFILL
CECIL COUNTY, MARYLAND

FIGURE

1A

Woodlawn Landfill
Vinyl Chloride and Sodium (- - -)
F-6

Vinyl Chloride Concentration (µg/L)

Vinyl Chloride Cleanup Level

• Detected Concentration

○ Detection Limit (constituent not detected)

TIME

Sodium Concentration (µg/L)

HISTORICAL TRENDS OF VINYL CHLORIDE
AND SODIUM FOR WELL F-6

WOODLAWN LANDFILL
CECIL COUNTY, MARYLAND

FIGURE

1B

Woodlawn Landfill

Vinyl Chloride and Sodium (- -)

F-7

Vinyl Chloride Concentration (µg/L)

Sodium Concentration (µg/L)

TIME

Vinyl Chloride Cleanup Level

Filename: VCNA1.TT3

• Detected Concentration
o Detection Limit (constituent not detected)

TTPLOT3 version 2.0

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Environmental and Infrastructure
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HISTORICAL TRENDS OF VINYL CHLORIDE AND SODIUM FOR WELL F-7

WOODLAWN LANDFILL
CECIL COUNTY, MARYLAND

FIGURE

1C

AR309674

Woodlawn Landfill
Vinyl Chloride and Sodium (- - -)

F-10

Vinyl Chloride Concentration (µg/L)

Sodium Concentration (µg/L)

TIME

Vinyl Chloride Cleanup Level

● Detected Concentration
○ Detection Limit (constituent not detected)

filename VCMA L F13

TTPLOT3 version 2.0

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HISTORICAL TRENDS OF VINYL CHLORIDE AND SODIUM FOR WELL F-10

WOODLAWN LANDFILL
CECIL COUNTY, MARYLAND

FIGURE
1D

DWG. DATE: 6/3/97 | PRJCT NO.: | HARD FILE: | DRAWING: | CHECKED: | APPROVED: | DRAFTER: MNGTH

AR309675

Vinyl Chloride Loss during Laboratory Holding Time

Richard Soule, Daniel Symonik,[1] David Jones,[2] Doug Turgeon, and Betsy Gerbec

Minnesota Department of Health, 121 E. 7th Place, St. Paul, Minnesota 55101

Because vinyl chloride is a potent human carcinogen, it is important that analytical results from groundwater samples accurately reflect levels of exposure to groundwater users. This study investigated the current allowable holding time of 14 days to determine if vinyl chloride is lost from samples during this time. Samples containing an initial concentration of 2 μg/liter of vinyl chloride showed progressive, increasing losses when held for 1, 2, 7, and 14 days. Due to the inherent variability of low-level laboratory results, the most statistically significant loss ($\alpha = 0.05$) was seen for samples held for 14 days. No statistically significant differences in degradation pattern were noted between analytical detectors used (PID versus Hall) or sample type (lab versus field). There also was a loss of vinyl chloride observed during sample collection and handling. These results suggest that analytical variability at low concentrations and the establishment of health-based guidelines near the analytical detection limit require multiple samples be collected from a single location when highly accurate results are needed. These findings should be considered in public health exposure assessments and the implementation of health-based recommendations at sites with vinyl chloride groundwater contamination. © 1996 Academic Press, Inc.

INTRODUCTION

Vinyl chloride is a potent human carcinogen and a common groundwater contaminant near hazardous waste sites. The guidelines for drinking water supplies containing vinyl chloride in Minnesota (USEPA, 1993; MDH, 1994) are nearly equivalent to typically reported analytical detection limits (ATSDR, 1993). Vinyl chloride has been found at 458 of the 1300 federal Superfund sites (ATSDR, 1993) and is commonly identified at levels above its regulatory guidelines. Efforts to protect users of aquifers contaminated by vinyl chloride

rely on analytical results to estimate human exposure. This makes it important to confidently determine that analytical results accurately reflect levels of vinyl chloride exposure.

The U.S. Environmental Protection Agency (USEPA) recommends that preserved water samples tested for vinyl chloride be analyzed within 14 days of collection (USEPA, 1988). In our experience, water samples analyzed immediately after collection seemed consistently higher than similar samples that were held for longer periods. This raised the concern that samples which are held for even a small portion of the holding time may underestimate both the vinyl chloride concentration and the potential human exposure. This, in turn, could result in an underestimation of the health threat to users of contaminated groundwater. The objective of this study was to determine if a significant amount of vinyl chloride was lost from water samples during the 14-day holding period.

METHODS
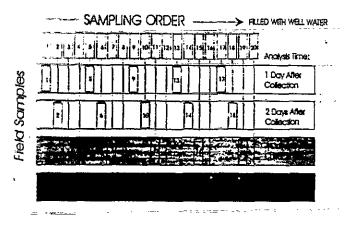
Two types of water samples were tested: laboratory-prepared water containing a known concentration of vinyl chloride ("lab samples") and groundwater samples collected from a single well ("field samples"). As an extraction well for a groundwater treatment system, this well is pumped continuously and has historically yielded groundwater consistently containing low part per billion levels of vinyl chloride. The concentration in the lab samples was chosen to be similar to those recently found in the well (1.5 μg/liter).

As shown in Fig. 1, three replicates of 20 field samples and 20 lab samples were collected in clean 40-ml glass vials with Teflon-lined septa. Samples within a replicate were numbered corresponding to their order of filling. Sampling procedures followed the techniques typically used in environmental investigations (MPCA, 1986). All samples were preserved with a biocide, adjusted to pH less than 2, and immediately refrigerated at 4°C until testing.

Both the field and lab samples were systematically assigned to four different holding time groups. Groups of five field samples and five lab samples each were
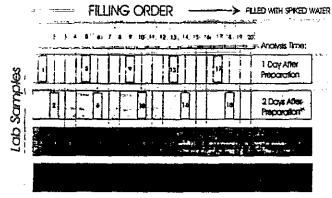
FIG. 1.   Sampling procedure.

FIG. 2.   Percentage loss over holding time.

analyzed at 1, 2, 7, and 14 days after collection (Fig. 1). Laboratory internal control samples consisted of laboratory standards and spiked samples. Blank and matrix spike data did not show sample contamination or a significant matrix effect on instrument performance.

Each sample was analyzed for vinyl chloride using both a photoionization detector (PID) and a Hall detector (Hall). Data from each detector were reported and compared separately using Student's t test. A Tracor 540 gas chromatograph was used along with a Tekmar TURBOcool option and EPA method 502.2 (USEPA, 1989). Chromatographic conditions were Restek Corp. 105-m × 0.53-mm-i.d. column with 3-μm film, trap temperature during purge at $-20°C$, trap packing Supelco Vocarb 3000, and purge time of 3 min; column program was initially at 40°C for 10 min, then 10°C per minute to 200°C, and held for 5 min.

RESULTS

The percentage loss of vinyl chloride for the lab and field samples versus holding time is plotted in Fig. 2. Data from replicates were combined to yield a data set of 15 samples ($n = 15$) for each detector and sample holding time group. Approximately 40% of the vinyl

chloride initially present was lost over the entire 14-day holding time, with roughly half (25%) of the loss occurring in the first 2 days. The decrease in vinyl chloride concentrations observed is statistically significant ($\alpha = 0.05$). The same trend of vinyl chloride loss was observed for both types of analytical detector.

The standard deviations of the combined results ranged from 0.02 to 0.17 μg/liter for the lab samples and from 0.07 to 0.29 μg/liter for the field samples. Daily standards prepared in the lab showed similar variability, suggesting that most of the variability was a result of the analytical methods (rather than a result of sample handling). This high degree of relative variability is common for vinyl chloride samples analyzed in this range and may raise concerns about the reliability of using a single sample to make public health determinations.

Figure 3 shows an analysis of concentration versus filling order. The major cyclical trend is due to the varying holding times for sequential sample bottle numbers. The figure suggests that there may be two other types of vinyl chloride loss occurring during the holding
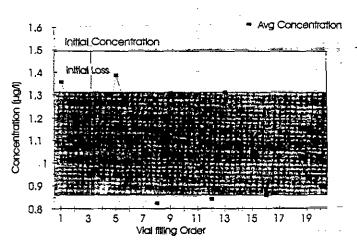
FIG. 3.   Types of losses.

time: (a) an initial loss of about 0.22 μg/liter (15%) that affects the results from all sample vials, regardless of origin or detector; and (b) a progressively increasing handling loss of up to 0.15 μg/liter (10%) which is shown by the regression line. The initial loss could only be determined using laboratory samples where the initial concentration is known (prepared spike). This portion of the loss may be laboratory related, such as measurement error, handling or headspace loss, or a factor common to all samples such as binding to glass, photodegradation, or loss through the septa. The handling loss is likely a result of increasing duration of sample exposure to air with increasing sample number (e.g., water in vial 20 was exposed to air longer and showed a greater loss than water in vial 1 since each was poured from the same supply).

DISCUSSION

Health-based standards for vinyl chloride are very low because it is rated as a Class A carcinogen with a relatively high estimated oral cancer slope factor of 1.9 (mg/kg/day)$^{-1}$ (USEPA, 1994). The U.S. EPA Maximum Contaminant Level, which is the value used for vinyl chloride in municipal water supply systems, is 2 μg/liter (based on the analytical detection limit; USEPA, 1993). The Minnesota Department of Health (MDH) has established a health-based guideline for private drinking water supplies of 0.2 μg/liter (based on cancer potency slope and a 10^{-5} risk; MDH, 1994). These standards are roughly equivalent to reported analytical detection limits in water (ATSDR, 1993). Due to the decrease in precision which occurs as concentrations approach the detection limit, accurate estimates of ambient water concentrations from a single sample are more difficult to obtain at lower concentrations.

The physicochemical characteristics of vinyl chloride and its environmental fate may eliminate several possible explanations for the observed loss. Although vinyl chloride has a very high saturation vapor pressure (2530 mm Hg at 20°C) and is subject to partitioning into an air head space [Henry's Law Constant of 1.2 (atm-m^3)/mol at 10°C], all samples were thoroughly checked to ensure that any air bubbles were removed. Although under certain circumstances vinyl chloride readily biodegrades (ATSDR, 1993), this pathway seems unlikely given that all samples were acidified and treated with biocide. The samples were kept in a darkened refrigerator to minimize photochemical degradation (EPA, 1986). Sorption of some organic chemicals onto the materials of sample containers has been observed (Bradbury et al., 1987), but the low octanol–water partitioning coefficient (log K_{ow} = 1.36) for vinyl chloride indicates that this would be negligible for the concentrations used in this study (per equation 5.8.4 in Manahan, 1994).

The most common source of vinyl chloride in ground-water at hazardous waste sites is the anaerobic dehalo-genation of 1,1,2-trichloroethene, tetrachloroethene, and 1,1,1-trichloroethane (ATSDR, 1993). Therefore, it can be present in groundwater at sites where pure vinyl chloride was not used or disposed and may be overlooked when developing a list of contaminants of concern. In addition, if an analytical technique is used which has a detection limit above 2 μg/liter, a significant complete exposure pathway may be missed and potential risks from a site underestimated.

Since significant public health actions, such as imposing drinking water restrictions or installing expensive treatment/removal systems, often hinge on limited analytical results, it is crucial to obtain the most accurate and precise measurements possible. For vinyl chloride, this can be accomplished by collecting more than one sample from a well, taking care to ensure that sample contact with the air is minimized, and using sufficiently sensitive analytical techniques. It is important for both risk assessors and risk managers to recognize the uncertainties in sample collection and analysis when dealing with analytical data from groundwater drinking water supplies potentially contaminated with vinyl chloride.

CONCLUSIONS

A statistically significant amount of vinyl chloride was lost from water samples between the time of collection and analysis. This loss increased to 40% of the initial concentration when held for 14 days prior to analysis. Therefore, immediate testing of samples is warranted where low part per billion concentrations of vinyl chloride may be present in drinking water (e.g., when concentrations may be near health-based standards). Moreover, the results of immediate analyses are more representative of actual exposure concentrations than those from samples held for longer times.

In addition to loss during holding time, this study suggests that there may be significant loss of vinyl chloride due to the sampling and handling processes. Therefore, sampling and analysis techniques should be reviewed to minimize sample exposure to the air.

Due to analytical variability at low concentrations, collection and analysis of multiple water samples from a single location are also warranted when highly accurate results are needed (e.g., when sample concentrations are near health-based guidelines or the analytical detection limit).

Since significant public health actions, such as imposing drinking water restrictions or installing expensive treatment/removal systems, often hinge on limited analytical results, it is crucial to obtain the most accurate and precise measurements possible. Both risk assessors and managers need to be aware of the uncertainty associated with reported vinyl chloride results in

order to make informed and appropriate public health decisions.

Although vinyl chloride was lost from samples, this study does not identify the mechanism of the loss. Some possible explanations may be volatilization (either into ambient air during sampling and analysis or directly through the sample bottle septa), microbial breakdown in the natural water, or chemical degradation. Additional analysis is currently being conducted to further characterize the mechanism of the observed loss.

ACKNOWLEDGMENTS

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Thanks to MN for their fine work.

A recent synopsis of a Minnesota study that appeared in Hazardous Substances
& Public Health (vol 6, #3, Fall 1996) indicates that water samples tend to
loose vinyl chloride with increasing holding time.   According to the
article, approximately 40% can be lost if a 14-day holding time is used and
up to 25% may be lost of held for 2 days before the sample is analyzed.
 These losses seem to be most significant at low ppb range, around the MCL
of 2 ug/l (ppb).

Because of these losses, I suggest that health assessors, for screening
purposes, DOUBLE any concentrations of vinyl chloride ranging between 1
and 50 ug/l as a first step in their overall analysis of drinking water
(and possibly soil gas and indoor exposures). If the doubled value exceeds
a relevant comparison value, the health assessor should then examine
carefully the QA/QC procedures including length of time the samples were
held, concordnce of any duplicate samples that may have been taken, etc.

As always, assessment of public health implications must go beyond simple
comparisons to levels in a medium or media. However, it is important for
the health assessor, the communities, ATSDR's partners (EPA, etc), to know
that ATSDR is aware of the possibility that some loss of contaminat has
been accounted for in the overall analysis.

Please feel free to comment or to put forward additional suggestions.

as

A scientific basis for revising regulatory holding times for VOC water samples

By O.R. West, D.W. Bottrell, C.K. Bayne,
R.L. Siegrist, and W.H. Holden
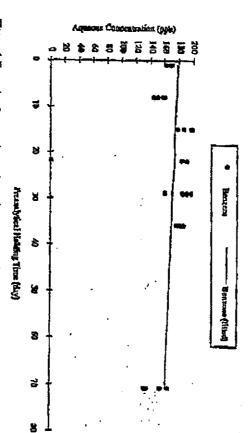
ANALYTE STABILITY during prema- nalytical storage is essential to the accurate quantification of contaminant levels in environmental samples. This is particularly true for volatile organic compound (VOC) analysis, since some of these target analytes can volatilize and/or degrade during sample storage. To reduce the impact of these transformation mechanisms on VOC analyses, regulatory agencies require that water samples be collected without headspace in 40-mL vials with polytetrafluoroethylene)-lined septum caps, acidified to pH ~2, and stored at 4 °C. Furthermore, analytical data are considered valid only if the analyses are conducted within 14 days of sample collection (7 days if the samples are not acidified). This maximum holding time was arbitrarily set and specified in 40 CFR Part 136[1] and has since been adopted by other regulatory programs and for application to other environmental media.[2] The appropriateness of this requirement must be reevaluated to assume compliance with this 14-day holding time has been difficult and costly for sample collectors, data users, and analytical laboratories. Recent Superfund Guidance[3] has attempted to address the problem by relying on data validators' judgement to assess the impact of missed holding times on analytical measurements. However, this has

space, 4 °C storage) are stable for time periods well over 14 days. The goal of this study was to confirm these previous studies, as well as to provide regulatory agencies with the data necessary to extend the maximum holding time for properly preserved VOC water samples to 28 days.

Experimental methods

The stability study was performed on surface water collected from a tributary of the Clinch River in Oak Ridge, TN. Water samples were prepared following the procedure described by Maskarinec, et al.[5] A clean

Table 1

Figure 1 Example of regression performed on concentration versus holding time data (data shown are for benzene).

Summary of linear regression on stability data for select compounds

Sample set W1	No. of data points	Regression parameters Intercept (ppb)	Regression parameters Slope (1-unit/day)	Significant negative slope (1-sided 5% significance)	Relative mean error	Change in conc. at 28 days (ppb)	% Change in conc. at 28 days
Acetone	18	21.2	0.0194	No	10%	—	—
Benzene	29	16.1	0.0038	No	9%	—	—
Carbon disulfide	28	15.2	-0.0501	Yes	8%	-1.4	-9%
Carbon tetrachloride	26	16.6	-0.0168	Yes	8%	-0.5	-9%
Chlorobenzene	26	16.8	-0.0154	Yes	8%	-0.4	-2%
Chloroform	26	18.0	0.0056	No	6%	—	—
Dichloroethene, trans-1,2-	26	15.8	-0.0211	Yes	5%	—	—
Methylene chloride	28	17.5	-0.0007	No	5%	-0.5	-4%
Pentanone, 4-methyl-2-	24	18.3	0.0082	No	7%	—	—
Styrene	28	17.7	0.0006	No	12%	—	—
Trichloroethane				No			-10%

...its requirement must be reevaluated because compliance with this 14-day holding time has been difficult and costly for sample collection, data users, and analytical laboratories. Recent Superfund Guidance[3] has attempted to address the problem by relying on data validators' judgment to assess the impact of missed holding times or analytical measurements. However, this has still led to unequivocal rejection of data when prescribed holding times are missed, and more specific guidance backed by scientific data is needed from regulatory agencies.[4]

Previous stability studies[5,6] have demonstrated that a majority of purgeable VOCs in properly preserved VOC water samples (acidified, no head-

Compound						
Acetone	16	21.2	0.0124	No	10%	—
Benzene	28	16.1	0.0033	No	5%	—
Carbon disulfide	28	15.2	-0.0501	Yes	6%	-9%
Carbon tetrachloride	28	16.6	-0.0189	Yes	6%	-3%
Chlorobenzene	28	16.8	-0.0134	Yes	5%	-2%
Chloroform	28	18.0	0.0059	No	6%	—
Dichloroethene, trans-1,2-	28	16.6	-0.0211	Yes	5%	-0.5
Methylene chloride	28	17.5	-0.0007	No	5%	-4%
Pentanone, 4-methyl-2-	24	18.3	0.0032	No	7%	—
Styrene	28	17.7	0.0069	No	12%	—
Tetrachloroethene	28	18.1	-0.0054	Yes	9%	-1.8
Toluene	28	16.2	-0.0095	No	6%	—
Trichloroethane, 1,1,1-	28	16.6	0.0034	No	8%	—
Trichloroethene	28	16.9	-0.0103	No	5%	—
Vinyl acetate	20	23.5	-0.3480	Yes	21%	-42%
Vinyl chloride	24	10.9	0.0915	No	43%	—
Xylene, m,p-	28	37.4	-0.0752	Yes	10%	-6%
Xylene, o-	28	18.7	0.0068	No	11%	—
Sample set W2						
Acetone	16	194.5	-0.2472	No	8%	—
Benzene	27	177.7	-0.2523	No	10%	—
Carbon disulfide	27	200.8	-1.2258	Yes	6%	-17%
Carbon tetrachloride	27	169.0	-0.6788	Yes	13%	-19
Chlorobenzene	27	182.0	-0.3497	Yes	6%	-10.9
Chloroform	27	194.0	-0.3069	Yes	6%	-8.8
Dichloroethene, trans-1,2-	27	176.5	-0.5869	Yes	9%	-18
Methylene chloride	27	179.3	-0.1591	No	9%	—
Pentanone, 4-methyl-2-	23	210.6	-0.0875	No	5%	—
Styrene	27	174.7	-0.5091	Yes	5%	-17.9
Tetrachloroethene	27	185.5	-0.5285	Yes	8%	-25.9
Toluene	27	178.8	-0.1986	No	16%	—
Trichloroethane, 1,1,1-	27	162.9	-0.5152	Yes	12%	-14.4
Trichloroethene	27	189.7	-0.5018	Yes	11%	-14.1
Vinyl acetate	18	235.4	-3.5267	Yes	19%	-42%
Vinyl chloride	23	144.0	-0.0049	No	19%	—
Xylene, m,p-	27	343.6	-1.1289	Yes	33%	-31.8
Xylene, o-	27	172.2	-0.4257	Yes	8%	-11.9

3-L polyvinyl chloride film bag was filled with 2 L of surface water. Measured aliquots of VOC standard solutions were injected into the water-filled bag through the bag's septum port. The bag was shaken for 1 min, and allowed to equilibrate at room temperature for 2 min. After equilibration, the spiked water was distributed into an appropriate number of pre-cleaned 40-mL VOA vials with PTFE-lined (0.010-in.-thick) silicone septum caps. Two hundred-fifty milligrams of NaHSO4 were placed in each vial prior to filling. Each vial was completely filled (i.e., with no headspace) and stored at 4 °C prior to analysis. Two sets of samples were prepared; one set was spiked to 20 ppb (W1) while a second set was spiked to 200 ppb (W2). At 1,8, 15, 22, 29, 35, and 71 days after sample preparation, four samples from each set were analyzed for VOCs. Analyses followed the purge-and-trap (PT) method,[7] except that all calibrations were performed in reagent water that had been acidified

Table 2.
Practical reporting time for compounds in concentration in sample sets W1 and W2; also includes relative change in concentration after 28 days of storage

Compound	Sample set W1 (20-ppb spike) Practical reporting time (days)	Sample set W1 % Change in conc. at 22 days	Sample set W2 (200-ppb spike) Practical reporting time (days)	Sample set W2 % Change in conc. at 28 days
Group 1: Practical reporting time greater than or equal to 28 days				
Acetone	71	—	71	—
Acrylonitrile	71	—	71	—
Benzene	71	—	71	—
Bromomethane	71	—	71	—
2-Butanone	71	—	71	—
Dichloroethane, 1,1-	71	—	71	—
Dichloroethane, 1,2-	71	—	71	—
Dichloropropane, 1,2-	71	—	71	—
Dichloropropene, 1,2-	71	—	71	—
Pentanone, 4-methyl-2-	71	—	71	—
Tetrachloroethane, 1,1,2,2-	71	—	71	—
Toluene	71	—	71	—
Trichloroethane, 1,1,2-	71	—	71	—
Vinyl chloride	71	—	45	—
Bromodichloromethane	43	—	71	—
Carbon tetrachloride	40	—	28	—
Chlorobenzene	71	—	34	—
Chloroethane	71	—	44	—
Chloroform	71	—	80	—
Oxidation	71	—	81	—
Trichloroethane, 1,1,1-	71	—	97	—
Methyl iodide	71	—	—	—
Group 2: Practical reporting time less than 28 days and % change at 28 days <10%				
Chloromethane	25	-5%	22	-10%
Bromomethane	25	-4%	20	-0%
1,1-Dichloroethene	50	—	20	-7%
trans-1,2-Dichloroethene	24	-4%	23	-0%
Ethylbenzene	40	—	80	-10%
Dichlorobenzene	—	—	25	-0%
Dibromochloromethane	—	—	25	-8%
m/p-Xylene	98	—	14	-0%
o-Xylene	71	—	14	-0%
Styrene	71	—	17	-7%
Bromoform	71	—	9	-10%
2-Hexanone	71	—	15	-6%
1,2,3-Trichloropropane	71	—	7	-9%
Group 3: Practical reporting time less than 28 days and % change at 28 days >10%				
Trichlorofluoromethane	18	-6%	12	-8%
Acrolein	—	—	14	-16%

initial concentrations. Out of 44 analytes, concentration changes exceeded 10% for only three compounds in W1: vinyl acetate (42%), cis-1,3-dichloropropene (11%), and trans-1,4-dichloro-2-butene (20%). Concentration changes exceeded 10% for a larger number of compounds in W2, including trichlorofluoromethane (15%), carbon disulfide (17%), acrolein (25%), cis-1,3-dichloropropene (14%), vinyl acetate (42%), cis-1,3-dichloropropene (12%), tetrachloroethene (16%), and trans-1,2-dichloro-2-butene (26%). Practical reporting times (PRTs) were calculated for each compound in each sample set following the method prescribed by Bayne et al. (Table 2). The compounds were subdivided into three groups—VOCs that have PRTs greater than 28 days (Group 1), VOCs that have PRTs less than 28 days, but for which the relative change in concentration on the 28th day was <10% of the initial value, and VOCs that have PRTs less than 28 days and the relative change in concentration on the 28th day was >10%.

Calculated PRTs were very short for those analytes with very low measurement variability, even through concentration changes on the 28th day were relatively small (e.g., styrene in W2: %RME = 5.0%, PRT = 9.4 days, percent change on the 28th day relative to initial concentration = –10%). In such cases, factors other than calculated PRTs should be considered when assessing the effects of holding times on measurement validity. Statistical definitions of significant concentration change, such as the practical reporting time approach, must be complemented with practical defini...

2) However, additional analytical problems for some of the latter compounds exist (e.g., inconsistent purging), which can confound the analytical process and cannot be addressed by restricting maximum holding times alone.

Conclusions

This study demonstrated that a 28-day holding time for properly preserved water samples would not jeopardize the measurement of VOCs. This holding-time extension would benefit the regulated community, particularly government agencies with large-scale compliance sampling programs such as the Department of Defense and Department of Energy. Stringent holding times result in logistical difficulties further complicated by additional requirements for sample screening (e.g., for radioactivity). The suggested modification of holding times can also increase the sample throughput of commercial laboratories through simplified sample management. Furthermore, application of this study's results to data review would improve the analytical data validation process by providing an alternative to the current practice of unconditional rejection of data if holding times are missed, a practice that is very costly but not technically defensible.

This study also demonstrated a methodology for conducting a stability study, and practical reporting time analysis of the stability data. The latter approach would be useful for establishing site-specific maximum holding times, which, depending on the compounds of interest, can be longer than 28 days.

trans-1,2-Dichloroethene	24				-4%
Ethylbenzene	40			20	-5%
Dibromochloromethane				25	-8%
m,p-Xylene	36			14	-6%
o-Xylene	71		17	9	-7% -10%
Styrene	71			15	-10% -6%
Bromoform	71				-6%
2-Hexanone	71			7	-6%
1,2,3-Trichloropropane	71			12	-6%

Group 3: Practical regarding time less than 28 days and % change at 28 days >10%

Trichlorofluoromethane	16	-8%	14		-15%
Acrolein	—	—	4		-25%
Carbon disulfide	18	-9%	8		-17%
Vinyl acetate	10	-42%	8		-42%
cis-1,3-Dichloropropene	12	-11%	13		-14%
trans-1,3-Dichloropropene	17	-9%	16		-12%
Tetrachloroethene	17	-10%	8		-16%
trans-1,4-Dichloro-2-butene	16	-20%	3		-28%

*Calculated following Ref 2. Set to 71 days for compounds with nonsignificant slopes.

Results

Regression lines were fitted to the data for concentration versus analysis day (e.g., *Figure 1*; see *Table 1* for regression parameters for a select number of compounds). Measurement variability (i.e., relative measurement error [%RMB]) for each compound within each sample set was estimated as follows:

$$\%RMB = \frac{S_0 \times 100\%}{C_0} \qquad (1)$$

where S_0 is the square root of the mean-square error for the linear regression residuals, and C_0 is the extrapolated concentration on Day 0. Calculated values for %RMB were predominantly less than 15% in both W1 and W2, with values...

to pH ~2 with reagent-grade NaHSO$_4$. Further experimental details are given in West et al.[1]

...uses being lower in W1 (20 ppb spike). These low values indicate that scatter in the data was generally minimal, and that concentration trends with time were less likely masked by measurement variability. Such masking of concentration trends may have occurred with vinyl chloride, which exhibited the highest %RMB in both sample sets (43 and 33%). Statistically insignificant changes in vinyl chloride concentration with time may have been due to large measurement variability. However, a statistically significant negative slope was observed in vinyl acetate in both W1 and W2, despite a relatively large %RMB (21 and 29%). For this compound, the concentration change with time was large enough to offset the masking effects of data scatter.

Changes in concentration after 28 days of storage (last column in Table 1) were predominantly low relative to the...

given the other sources of uncertainty in site characterization and risk assessment for which analytical data are typically used. Examples of these uncertainty sources included spatial and temporal validity of containment concentration, use of simplified transport models to approximate exposure pathways, and extrapolation of laboratory toxicity data from animals to humans.

Based on calculated PRTs and an acceptable concentration change of 10% for low-variability analytes, the stability study showed that the measurement of 36 of 44 purgeable VOCs in properly preserved water samples will not be affected by sample storage for 28 days. Larger changes in concentration (>10%) and low PRTs were observed for a few analytes (see Group 3 in Table...

change of 10% was chosen to assess holding time effects on compounds in this study. This criterion is reasonable given the other sources of uncertainty...

specifications for acceptable concentration changes should be tied into the eventual use of the analytical data. For example, acceptable concentration changes for analytical data used in quantitative risk assessments can be determined by the sensitivity of the risk assessment results to variations in the input analytical data. An acceptable change of 10% was chosen to assess...

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